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IRON-MnO_2 BATTERY

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Plastic bonded iron electrode is fabricated with ferrous sulphate as starting material. Manganese dioxide (γ-form) is used for the fabrication of the positive electrode. Alkaline iron-manganese dioxide is assembled with one negative plate and two positive plates. Charge-discharge is carried out. The results are presented in this paper. The limitations of the cellophane paper and nylon felt as separator materials for the iron-manganese dioxide rechargeable battery are clearly indicated.

Key words: Charge-discharge cycle, dendrite, hot pressed, polyethylene, polystyrene, electrolytic manganese dioxide, anode poisoning

INTRODUCTION

Manganese dioxide (γ-form) is a good depolariser or cathode material in electrochemical power sources known from the time of Leclanche, the inventor of the famous and widely used Zn-MnO_2 system. It is used in varieties of portable power sources in conjunction with zinc as the anode and ammonium chloride or alkali as the electrolyte. The cathodic reduction of MnO_2 in alkaline medium is supposed to proceed [1,2] through different steps as shown below:

$$MnO_2 + H_2O + e^- \longrightarrow MnO.OH + (OH)^-$$

$$MnO.OH + H_2O + e^- \longrightarrow Mn(OH)_2 + (OH)^-$$

$$2MnO_2 + H_2O + 2e^- \longrightarrow Mn_2O_3 + 2(OH)^-$$

The cathodic reduction of MnO_2 is thus complicated and further discharge reactions are not highly reversible. As a result, attempts made [3] to render the zinc-manganese dioxide alkaline system as a rechargeable system have resulted only in partial success with limited number of charge-discharge cycles and with low rate of charge-discharge. The zinc electrode also limits the performance of the rechargeable Zn- MnO_2 alkaline battery by virtue of the solubility of $Zn(OH)_2$ in alkali which leads to dendrite growth on the zinc electrode causing cell short while charging.

Iron as the battery anode in conjunction with MnO_2 cathode in alkaline medium has certain advantages over the zinc. Firstly, it is less eaxpensive than zinc. Secondly its discharge product viz. $Fe(OH)_2$ is insoluble in alkali whereas $Zn(OH)_2$ is soluble in alkali leading to shape change of the zinc electrode limiting the cycle life. Matsuhita Electric Industrial Company Ltd., Japan has developed different primary versions of Fe-MnO_2 alkaline batteries with good shelf life[4]. In the present work preliminary studies have been carried out on rechargeable Fe-MnO_2 alkaline battery and the results are presented in this paper. The discharge-charge reaction of the Fe-MnO_2 system is represented as

$$2Fe + 3MnO_2 + 2H_2O \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Mn_3O_4 + 2Fe(OH)_2$$

Anode or negative electrode fabrication

The negative electrode is a porous sintered iron plate or a conducting plate with a mixture of iron and iron oxide powders held together with a plastic binder. On charge-discharge, finely divided iron powder and ferrous hydroxide, which are the anode active materials, are generated. The negative plate is fabricated from ferrous sulphate by adopting the following procedure.

Ferrous sulphate is purified by recrystallisation. It is then subjected to roasting at about 1173K until all the oxides of sulphur are completely removed. The iron oxide formed during roasting is heated again in H_2 atmosphere at about 973K to effect partial reduction. Using the partially reduced iron oxide the following mix is prepared:

Partially reduced iron oxide	...	66%
Sodium benzoate	...	20%
Polyethylene	...	5%
Sodium sulphide	...	2%
Mercuric oxide	...	2%
Copper powder	...	5%

The mix is then hot pressed onto both sides of a nickel plated mild steel mesh to a thickness of about 1.5 mm. The pressed plate is treated with boiling water to remove sodium benzoate which is a pore-former. The porosity of the resulting plate is about 55%. The dimension of the finished iron negative is 160(H) x 75(B) x 1.5(T)mm.

Cathode or positive electrode fabrication

Electrolytic manganese dioxide (EMD) is used to fabricate the positive electrode. The EMD (-200 mesh size) is mixed with 30% by weight of graphite powder. Water-soluble materials such as starch and cellulose (carboxymethyl cellulose) and water-insoluble materials like polystyrene have been tried to an extent of 5% as binders to press the plates. The plates pressed with carboxymethyl cellulose and starch as binders are of no use in practice since the active material comes out of the grid while charging whereas the plastic (polystyrene) bonded plate is found to be good to carry out the studies. The dimension of the finished positive plate is 160(H) x 75(B) x 1.5(T) mm.

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Cell assembly

The cell is assembled with one positive MnO_2 and two negative iron plates. Cellophane paper and nylon felt have been tried as the separator materials. The electrolyte is 30% KOH solution containing 15 g/l of LiOH.

RESULTS AND DISCUSSION

The cell assembled with two cellophone paper wrappings on the iron negative is subjected to charging at 2A up to 1.75V. The cell is discharged at 1A up to a cut-off voltage of 0.6V. The output realised is only about 45% of the Ah input. During charging, heavy gassing is observed on the positive electrode. As the charge-discharge is continued, the output starts falling down reaching a minimum after 10 cycles. At this stage the cellophane paper wrappings are found to be completly disintegrated.

The electrodes are washed well and again assembled with four wrappings of cellophane paper on the negative electrode. The charge-discharge is carried out. The charge-discharge behaviour is shown in Fig. 1. As in the previous case the output slowly decreases and the cell fails to give any output beyond 15th cycle. The slow decrease in the output and failure after sizeable period of operation is due to complete disintegration of the cellophane separator.

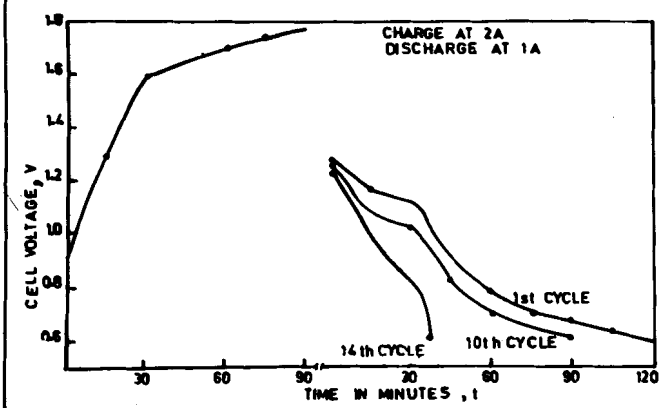

Fig. 1: Charge - discharge curves with cellophane paper as separator

The electrode assembly is washed well and set up again with 2 mm thick nylon felt as the separator. Charge-discharge is carried out as shown in Fig. 2. Here again, the output is fairly good in the beginning and it slowly decreases with cycling. The ampere-hour output reaches a minimum after 15 cycles. These studies clearly indicate that the cellophane separator fails due to physical disintegration in alkaline medium and the nylon felt, though it is physically intact, fails to prevent the migration of the soluble manganese salt from the positive electrode to the negative electrode leading to slow decrease in the output and subsequent failure. With the available separators, the electrochemical characteristics of the alkaline Fe- MnO_2 system are as follows:

Open circuit voltage	...	1.2V
Energy efficiency	...	45%
Charge-discharge cycles	...	40

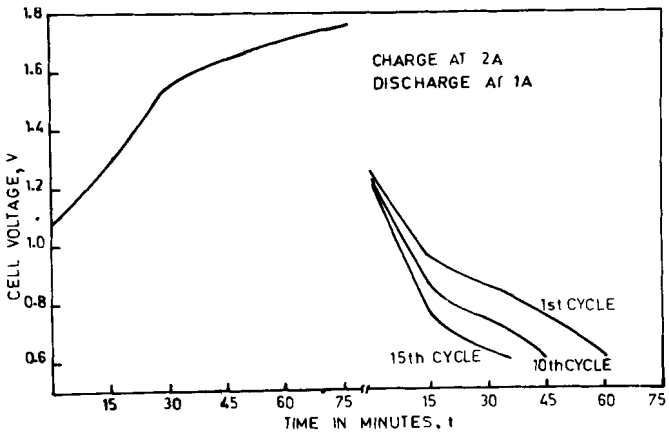

Fig. 2:Charge-discharge curves with nylon-felt as separator

CONCLUSION

The rechargeable Fe-MnO_2 battery is a low-drain system with an energy efficiency of about 45%. In order to make use of the system for practical applications, the currently available separators in India such as cellophane paper, nylon felt and microporous PVC are not suitable as some of them undergo physical disintegration in 30% potassium hydroxide solution and some fail to prevent the anode poisoning. An ideal separator must be the one that is alkali resistant and permeable to H^+ and $(OH)^-$ ions without allowing any other soluble ionic species as in the case of Ag/Zn battery separator. Such a separator is not commercially available in India at present. So the prerequisite for the development of the rechargeable Fe- MnO_2 alkaline battery is the development of separator meeting the above mentioned specifications. A common failure mode in Ag/Zn, Ni/Zn, Fe/O_2 and Fe/MnO_2 battery systems is due to anode poisoning which is caused by the migrating ions through the separator. Since KOH solution is the electrolyte in all these battery systems, the same material could serve as an effective separator which is alkali resistant, permeable to H^+ and $(OH)^-$ ions, and impermeable to other ions.

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